Upscaling Coupled Pore-Scale Reactive Transport Processes to the Continuum Scale

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OUTLINE

- **Motivation**
- **Multi-Scale Continuum Model**
- **Pore-Scale Models: Lattice Boltzmann & Pore Network Models**
- **Examples**
  - **Fracture Media**
  - **Structured Porous Media**
- **Conclusion**

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Reasons for Upscaling Pore-Scale to Continuum Scale

- Validate continuum model
  – Does simple volume averaging work?
  – Obtain continuum constitutive relations from pore-scale model

- Determine form of continuum model (single, dual, …) best suited for given porous medium

- Use pore-scale model to understand effects of multiscale processes at the continuum scale

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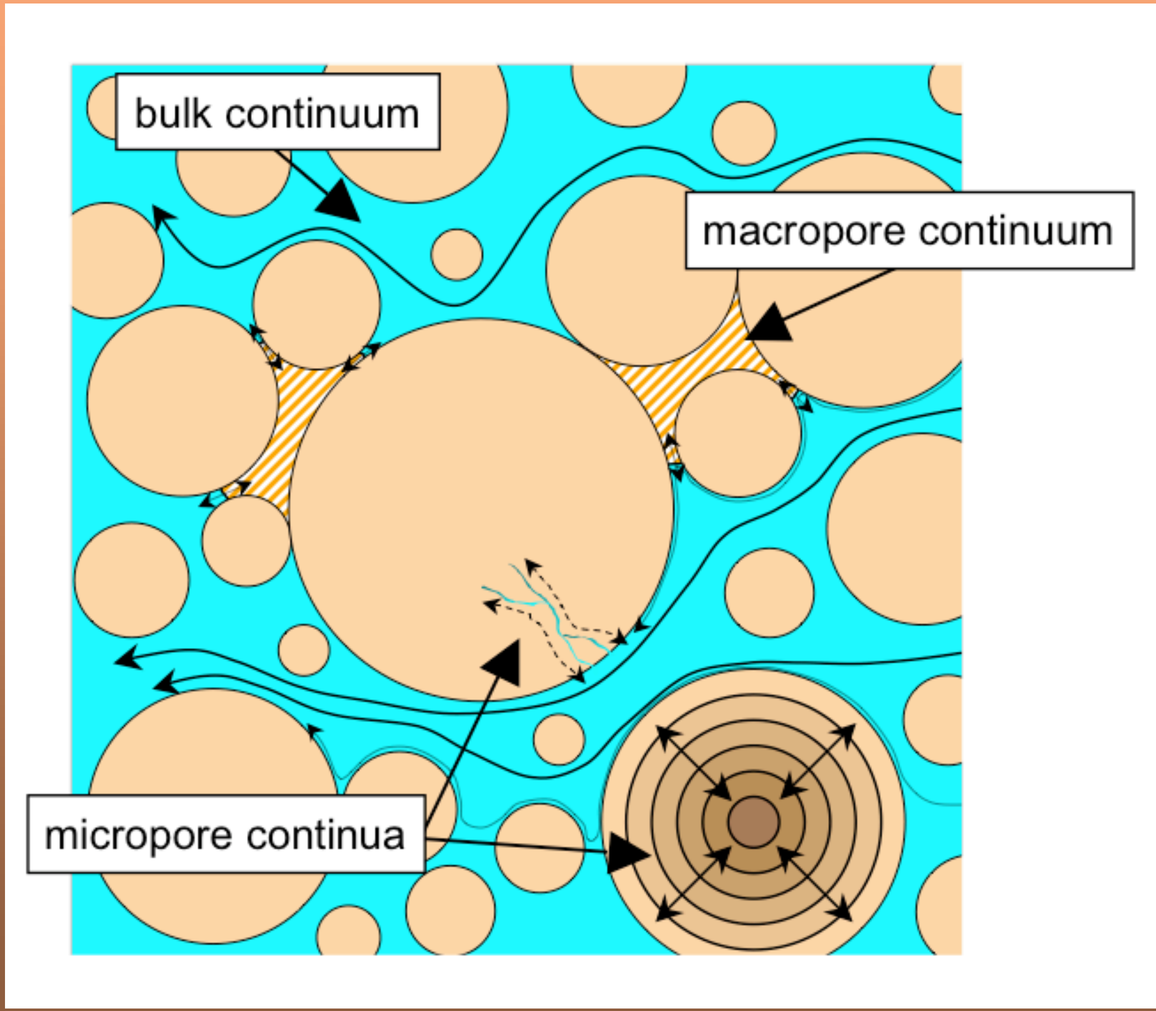
Multi-Scale Processes



Multi-Scale, Multicomponent Reactive Transport Equations

Primary (bulk) domain:

$$\frac{\partial}{\partial t}\left(\epsilon_b \varphi_b \Psi_j^b + S_j\right) + \boldsymbol{\nabla}\cdot \epsilon_b \boldsymbol{\Omega}_j^b = \sum_k A_{kb}\Omega_j^{kb} - \sum_s \nu_{js} I_s^b$$

Secondary (*k*th matrix) domain:

$$\frac{\partial}{\partial t}\left(\varphi_k \Psi_j^k + S_j^k\right) + \boldsymbol{\nabla}\cdot \boldsymbol{\Omega}_j^k = -\sum_s \nu_{js} I_s^k$$

Boundary condition and interfacial flux:

$$C_j^k(r = r_k,\, t; \boldsymbol{r}) \;=\; C_j^b(\boldsymbol{r},\, t), \qquad \Omega_j^{kb} \;=\; -\varphi_k D_k\left(\frac{\Psi_j^k - \Psi_j^b}{d_{kb}}\right)$$

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Pore-Scale Models

- **Pore-Network Model**
  - Abstraction of pore geometry: pore-scale heterogeneity unconstrained
  - Does not discretize pore space: pore-scale gradients not represented
  - Can handle larger domains compared to LBM
  - Treats minerals reactions through volume averaged rate

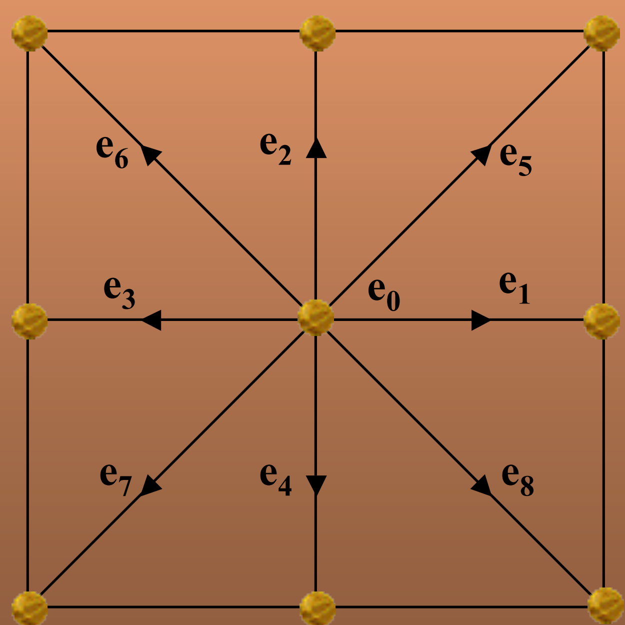
- **Lattice Boltzmann Model (LBM)**
  - Resolves individual pore space
  - Compute pore velocity (solves Navier-Stokes equations)
  - Treats mineral reactions as boundary condition at fluid-solid interface
  - Smallest practical resolution ~ 0.1 μm
  - Difficult to impossible to resolve solid phase at very small scales

DESCRETIZED FORM OF LBM FOR FLUID FLOW

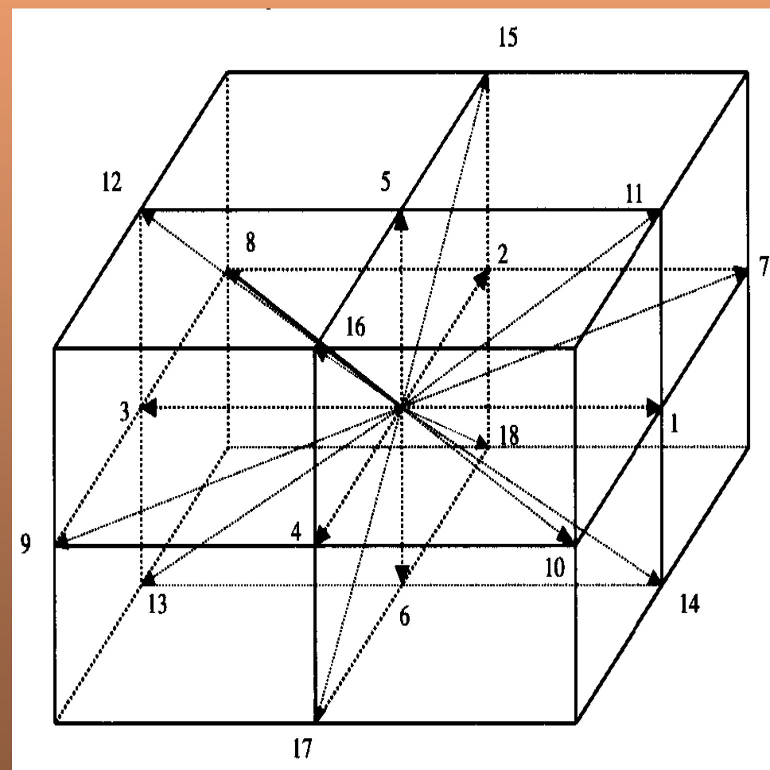
- **Evolution equation for particle distribution function**

$$f_\alpha(\boldsymbol{x}+\mathbf{e}_\alpha \delta t,\ t+\delta t) = f_\alpha(\boldsymbol{x},\ t) - \frac{f_\alpha(\boldsymbol{x},\ t) - f_\alpha^{\ eq}(\rho,\ \boldsymbol{u})}{\tau_f}$$

$$\rho = \sum_\alpha f_\alpha \qquad \rho \boldsymbol{u} = \sum_\alpha \boldsymbol{e}_\alpha f_\alpha$$



D2Q9 lattice



D3Q19 lattice

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LBM METHOD OF SOLUTION

- **Explicit Finite Difference**
  - Streaming $$f_i(\boldsymbol{x} + \boldsymbol{e}_i \delta t,\ t + \delta t) = f^*{}_i(\boldsymbol{x},\ t)$$
  - Collision $$f^*{}_i(\boldsymbol{x},\ t) = f_i(\boldsymbol{x},\ t) - \frac{f_i(\boldsymbol{x},\ t) - f_i^{eq}(\rho,\ \boldsymbol{u})}{\boldsymbol{\tau}_f}$$
  - Courant-Friedrichs-Lewy Condition $$\mathrm{CFL} = \frac{|\boldsymbol{e}_\alpha|\ \delta t}{\delta x} \leq 1$$
- **Equivalent to Navier-Stokes Equations**
- **Easily Parallelizable**

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LATTICE BOLTZMANN METHOD FOR MULTI-COMPONENT REACTIVE TRANSPORT

- **Evolution Equation for Particle Distribution Function**

$$g_{\alpha j}(\mathbf{x} + \mathbf{e}_\alpha \delta t,\ t + \delta t) = g_{\alpha j}(\mathbf{x},\ t) - \frac{g_{\alpha j}(\mathbf{x},\ t) - g_{\alpha j}^{eq}(C_j,\ \mathbf{u})}{\tau_{\text{aq}}}$$

- **Pore Scale Convection-Diffusion-Reaction Equation**

$$\frac{\partial \Psi_j}{\partial t} + (\boldsymbol{u} \cdot \nabla)\Psi_j - \nabla \cdot (D \nabla \Psi_j) = 0 \qquad \Psi_j = \sum_\alpha g_{\alpha j}$$

$$D = \frac{1}{3}(\tau_{\text{aq}} - 0.5)\frac{\delta l^2}{\delta t} \qquad \Psi_j = C_j + \sum_{i=1}^{N_{cx}} \nu_{ji} C_i (C_1, \cdots, C_{N_c})$$

- **Surface Reaction Boundary Condition**

$$\left.\begin{aligned} D\frac{\partial C_j}{\partial n} &= \sum_{i=N_c+1}^{N} \nu_{ji} I_i^* + \sum_{m=1}^{N_m} \nu_{jm} I_m^* \\ D\frac{\partial C_i}{\partial n} &= -I_i^* \end{aligned}\right\} \Rightarrow \begin{aligned} D\frac{\partial \Psi_j}{\partial n} &= \sum_{m=1}^{N_m} \nu_{jm} I_m^* \\ I_m^* &= -k_m \lambda_m (1 - K_m Q_m) \end{aligned}$$

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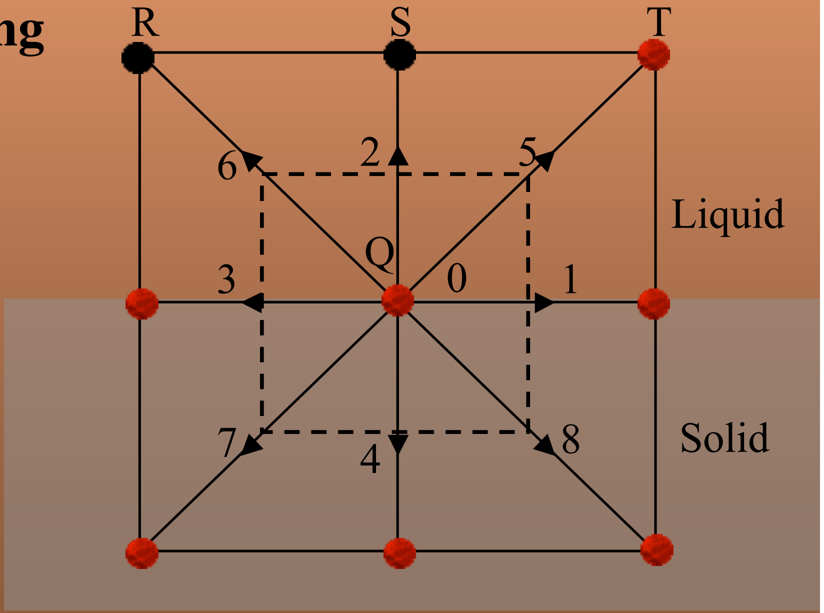
Moving Boundary Problem: Dissolution and Precipitation in LBM

- **Treat solid phase as continuum**
  - **More than one mineral may coexist at a single node**
  - **Solid concentration calculated using continuum-based equation:**

$$\phi_m(r_Q,\, t+\delta t) = \phi_m(r_Q,\, t) + \delta t \bar{V}_m a_m I_m^*(r_Q,\, t)$$

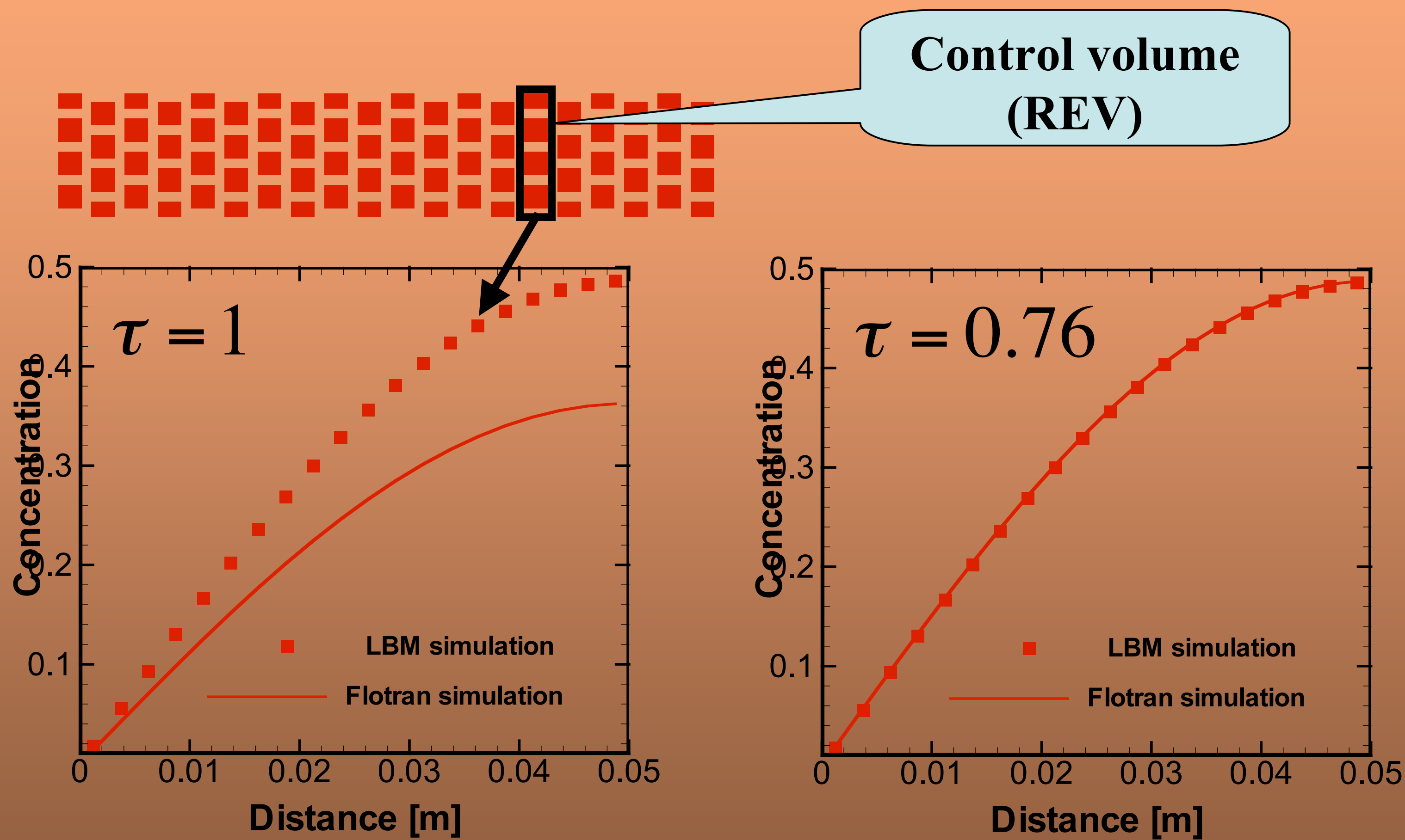
  - **Surface area a_m based on lattice spacing and may include roughness factor**



$\phi_m(r_Q,\, t+\Delta t) = 0$, node Q removed,

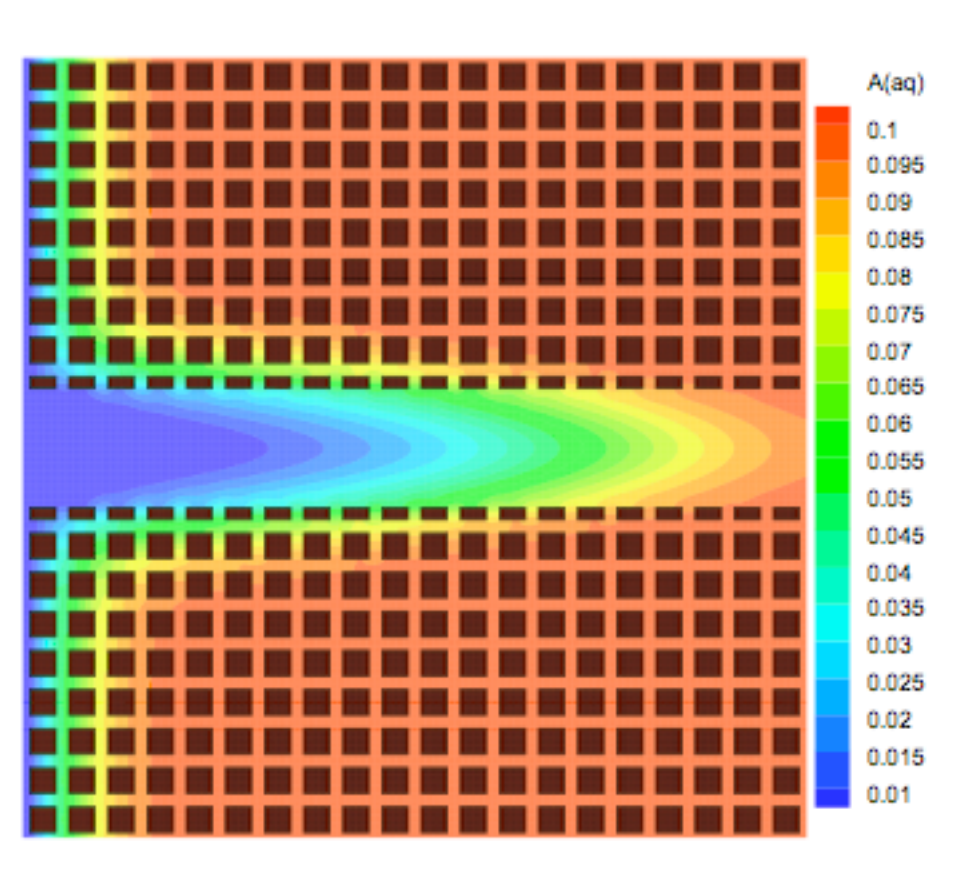
$\phi_m(r_Q,\, t+\Delta t) > 1$, node R, S or T randomly chosen to become solid node with probability ratio: $P_S = 4P_R = 4P_T$.

LBM Calculation of Tortuosity



Spatial distribution of concentration at time = 5.21 x 10^5 s

Fracture-Matrix Interaction



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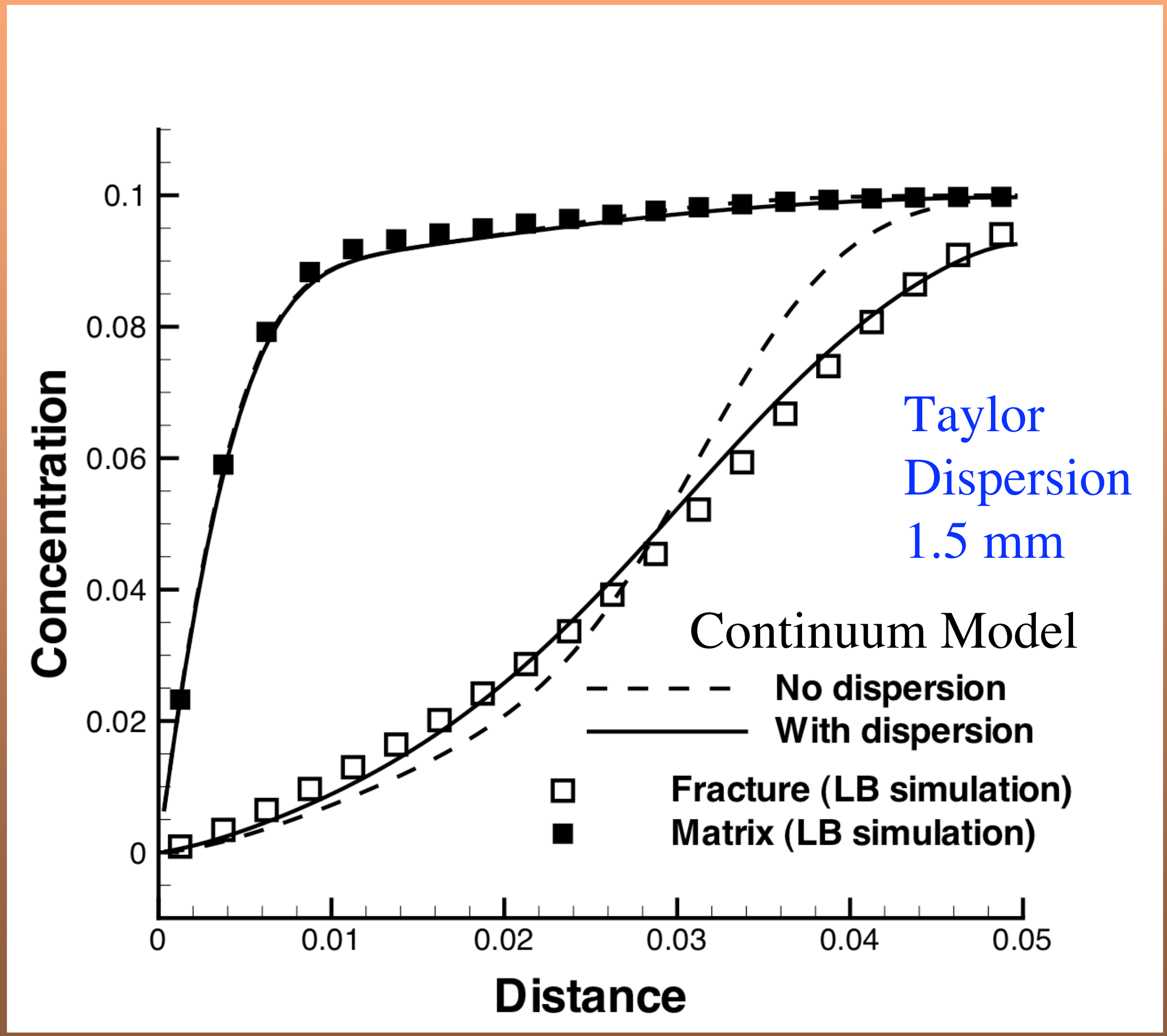
Discrete Fracture Model



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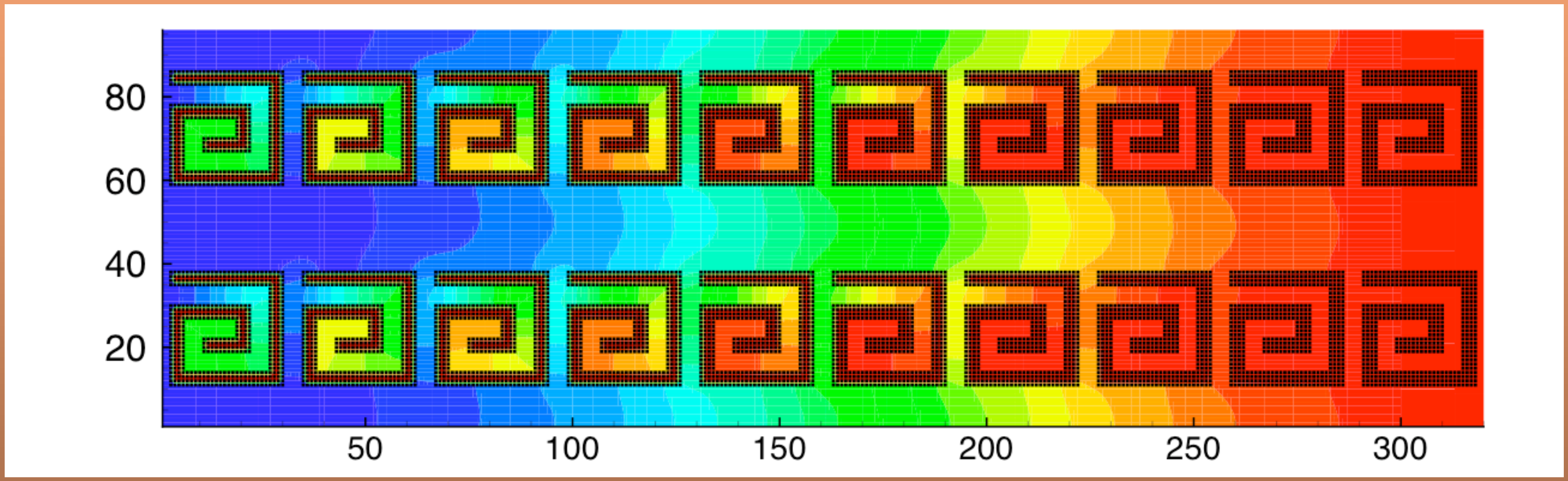
Example: Structured Porous Medium

FLOW

Tracer



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Model Geometry and Continuum Fit Parameters

Table 1: LB geometry and parameters for continuum model. One lattice unit equations 1.25×10^{-4} m.

Property	Symbol	Units	Bulk	Matrix
System Length	(L_b)	cm	4	—
System Width	(L_w)	cm	1.2	—
Matrix Block Size	(l_m)	mm	—	3.5
Channel Width	—	mm	—	0.5
Channel Length	—	mm	—	9.0
Bulk Volume Fraction	(ϵ_b)	—	0.4896	—
Porosity	(φ_b, φ_k)	—	1	0.367
Diffusivity	(D_b, D_k)	$m^2\ s^{-1}$	10^{-9}	8×10^{-10}
Specific Surface Area	(A_b, A_k)	cm^{-1}	5.625	15.10
Darcy Velocity	(q_b, q_k)	$m\ y^{-1}$	14.4	0

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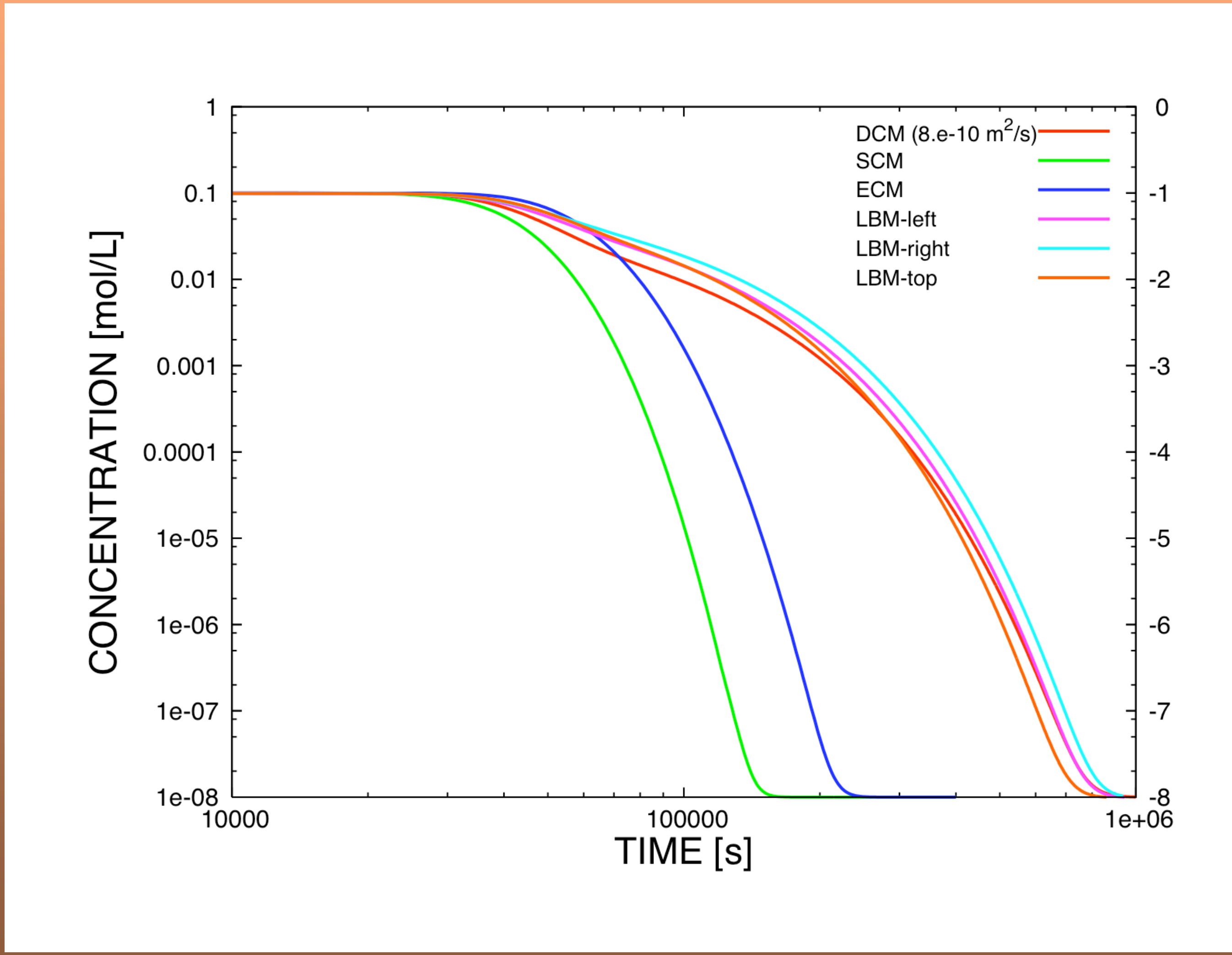
Comparison of Upscaled LB Model to Continuum Model (Tracer)



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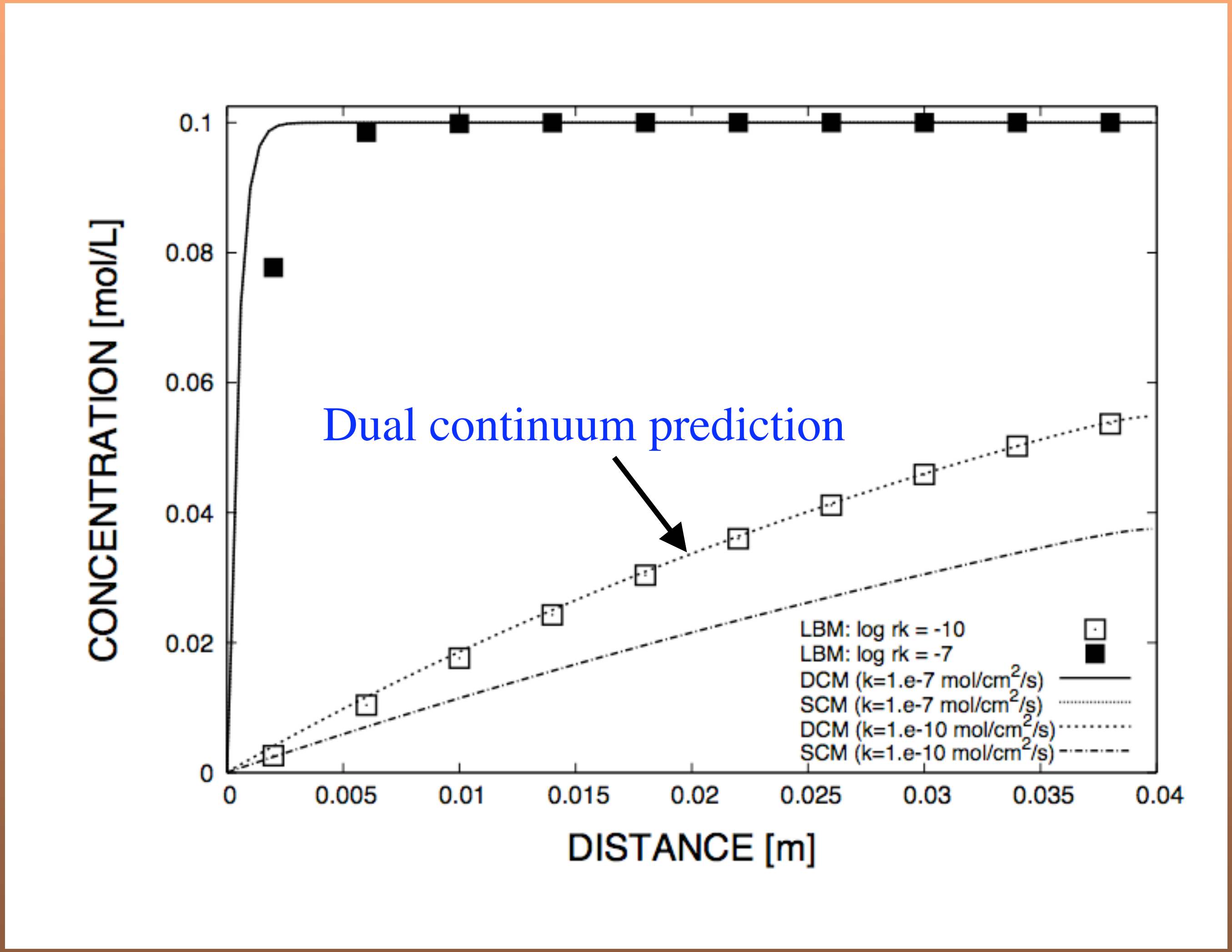
Linear Kinetics: Stationary State Dissolution



Equivalence of Dual and Single Continuum Models for a Single Component Stationary-State

- **Dual continuum stationary state transport equations:**

$$q\frac{dC_b}{dx} = -ka_b(C_b - C_{\text{eq}}) + a_{mb}\varphi_m D_m \frac{\partial C_m}{\partial y}\bigg|_{y=0}$$

$$-\varphi_m D_m \frac{\partial^2 C_m}{\partial y^2} = -ka_m(C_m - C_{\text{eq}})$$

$$C_m(y=0;\, x) = C_b(x)$$

- **Equivalent effective single continuum equation:**

$$q\frac{dC_b}{dx} = -ka_e(C_b - C_{\text{eq}})$$

$$a_e = a_b + a_{mb}\sqrt{\frac{a_m\varphi_m D_m}{k}}\left(\frac{1-\exp\left(-2l_m\sqrt{ka_m/\varphi_m D_m}\right)}{1+\exp\left(-2l_m\sqrt{ka_m/\varphi_m D_m}\right)}\right)$$

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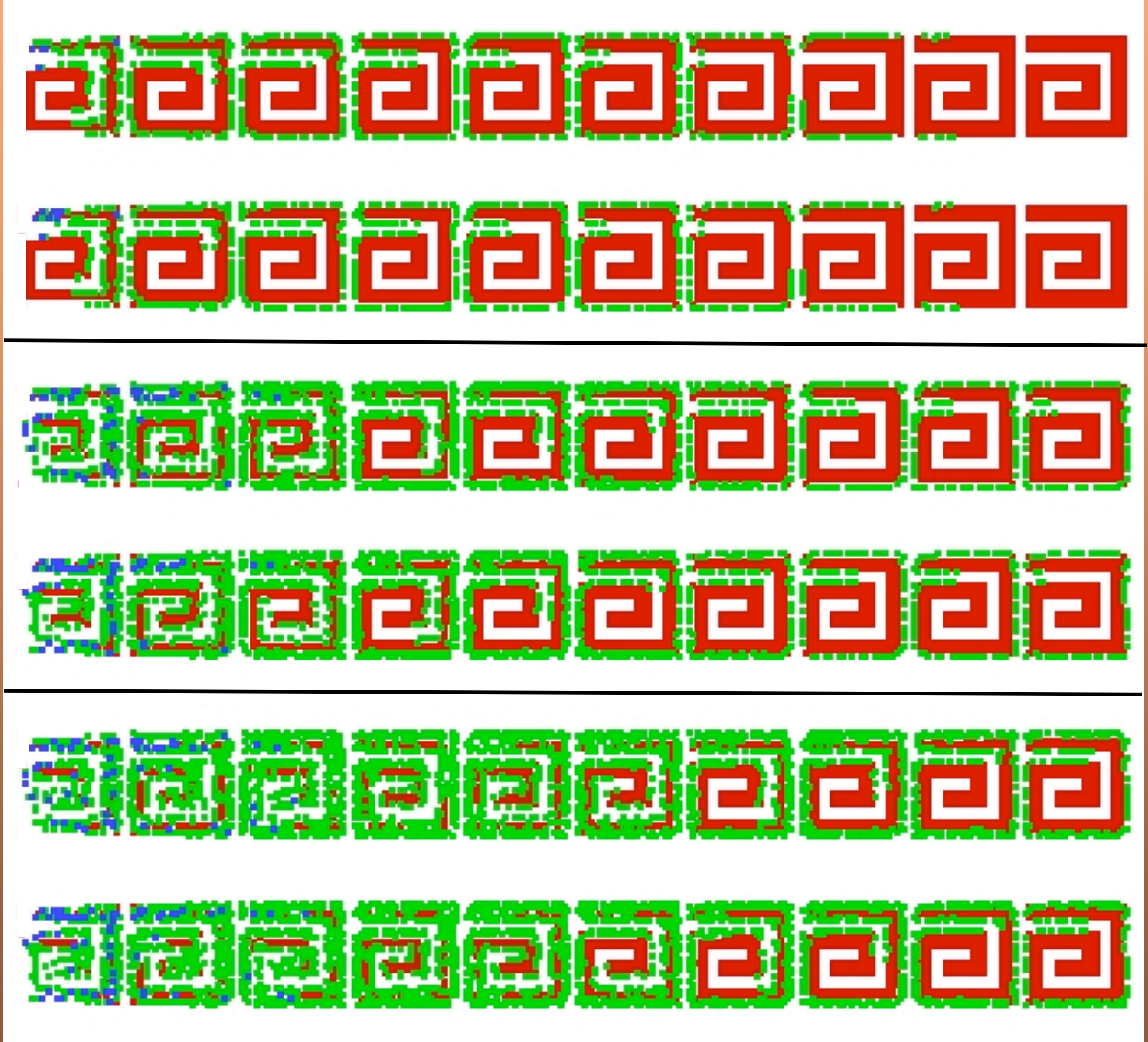
Multicomponent System: 100 bars CO_2 + Mg + SO_4 + Calcite → Dolomite + Gypsum

t = 10^5 steps

t = 2×10^5 steps

t = 4×10^5 steps



Calcite

Dolomite

Gypsum

1 LBM step = 0.026 s

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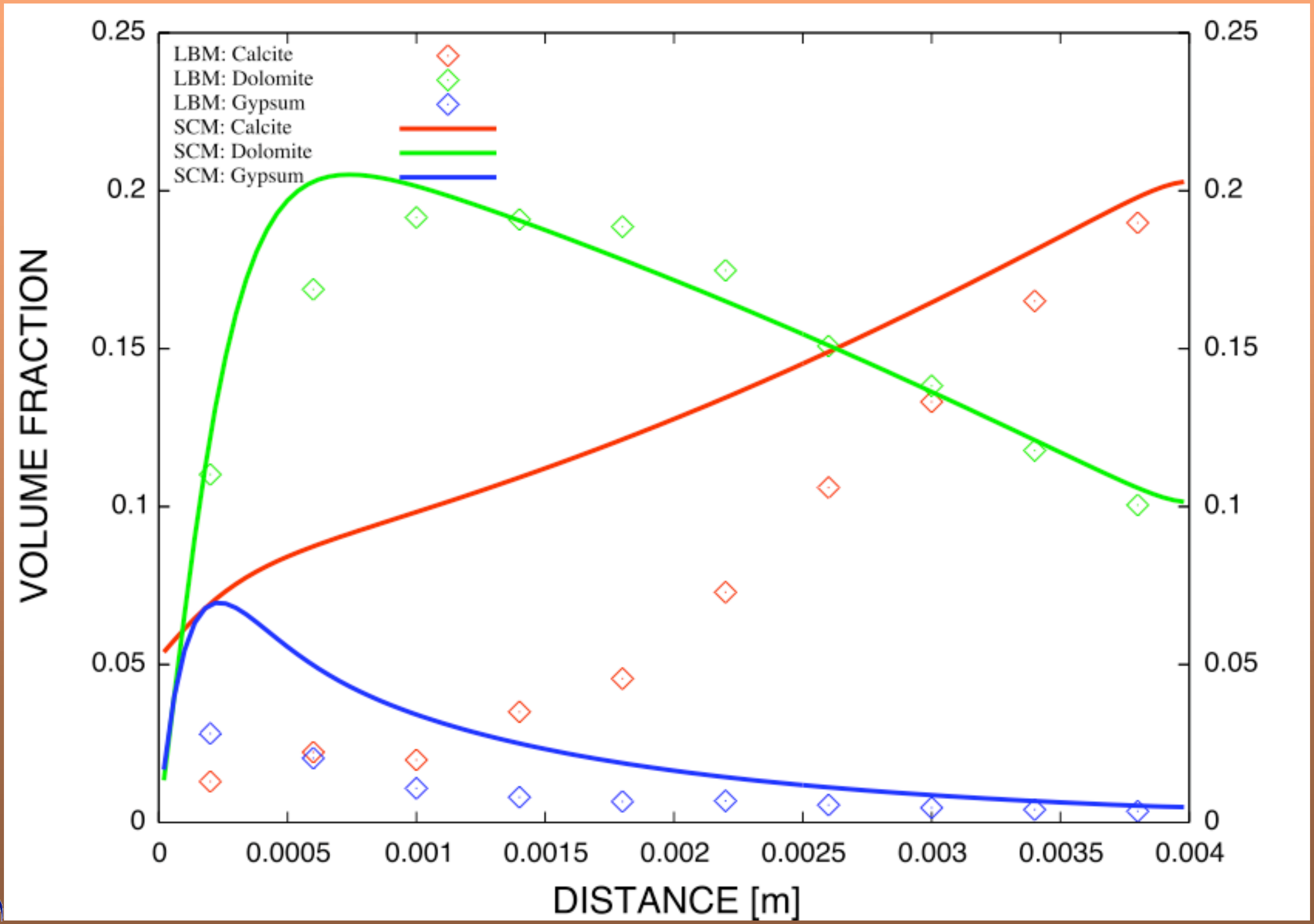
Comparison with Single Continuum Model



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Continuum and LBM Surface Areas

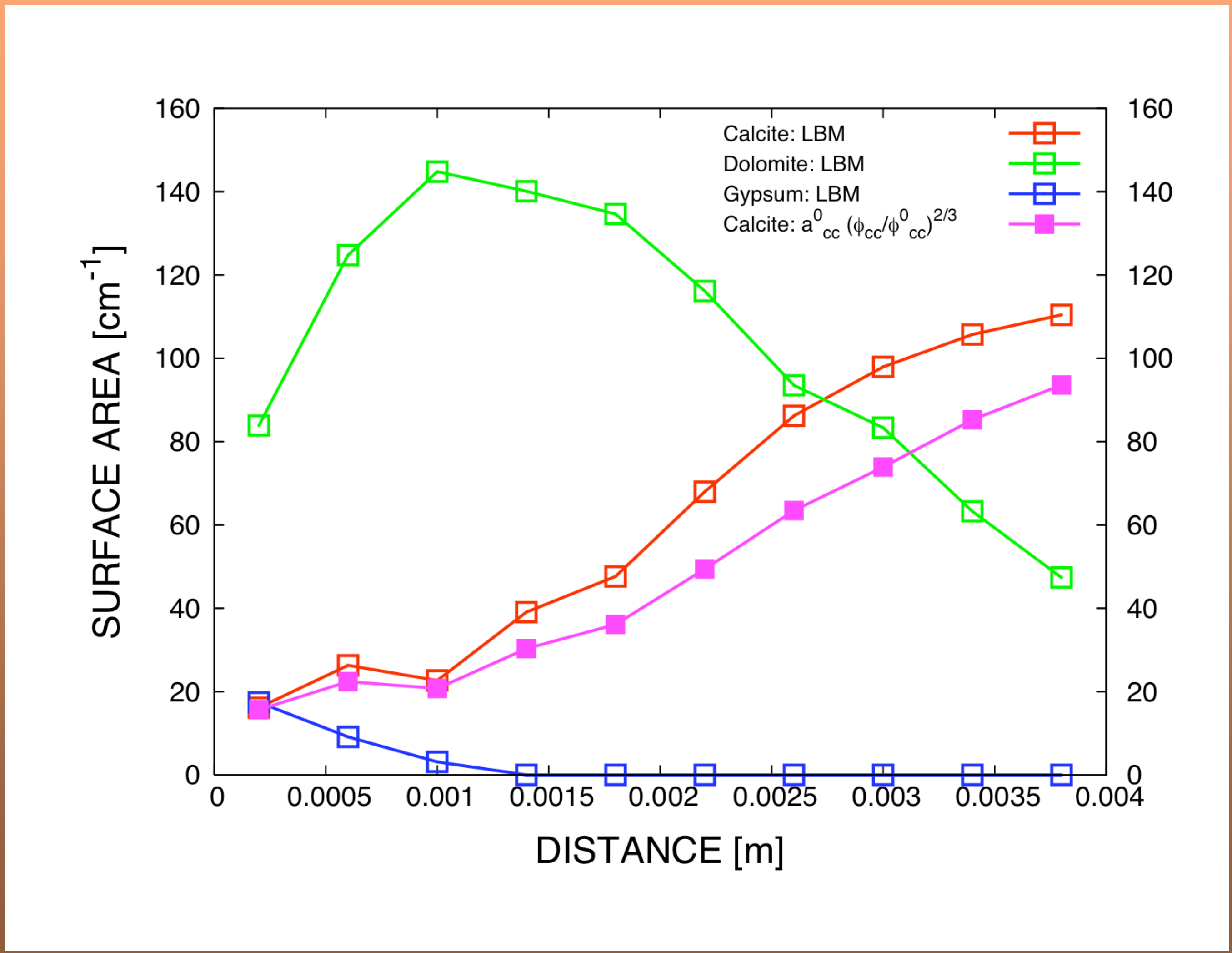
- **Continuum Model**
  - **Different surface areas for precipitation and dissolution**
  - **Surface evolution empirical:**

$$a_m = a_m^0 \left(\frac{\phi_m}{\phi_m^0} \right)^{2/3} \qquad \text{(Dissolution)}$$

$$= \text{constant} \qquad \text{(Precipitation)}$$

- **LBM**
  - **Surface area is determined by geometry and nucleation kinetics—surface area evolution related to rules for determining geometry evolution**

Upscaling LBM Surface Area



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Conclusions

- Multicomponent Lattice Boltzmann model developed with same chemistry as in continuum models with heterogeneous mineral reactions incorporated as boundary conditions at mineral surface.

- Pore-scale models can provide insight into upscaled continuum model formulations and provide parameter values for permeability, effective diffusivity (tortuosity), micro-scale dispersivity, reactive surface area etc.

- Generally a multi-scale continuum model is needed to fit a pore-scale simulation.

Conclusions [Continued]

- Main difficulty in applying LBM is quantifying pore-scale geometry, mineral distribution and associated surface area at micron (pore) scales.

Future Work

- Validate LBM and apply to realistic pore-scale geometries.

- Investigate upscaling pore-scale sorption processes: can sorption "kinetics" be explained by diffusion processes coupled to fast reaction kinetics in complex pore geometry?
  - Ion exchange
  - Surface complexation and charge balance
    - Nernst-Planck equation

- Evolving multiple continua
  - Weathering: continuous evolution of geometry from fractured (bed rock) to porous medium (saprolite)

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